



# National Institute of Standards & Technology

## Report of Investigation

### Reference Material 8852

#### Ammonium ZSM-5 Zeolite

This Reference Material (RM) is intended to provide a common source of ZSM-5 zeolite for measurement comparisons. The ammonium ZSM-5 zeolite was donated to the National Institute of Standards and Technology (NIST) by a zeolite-producing company. A unit consists of approximately 35 g to 40 g of material in a sealed container.

Reference and information values derived from chemical, diffraction and particle size measurements are provided in Tables 1 through 8.

**Reference Values:** Reference values are a best estimate of the true value provided by NIST where all known or suspected sources of bias have not been fully investigated by NIST [1]. Reference values for major components (major elements, loss on ignition [LOI], loss on fusion [LOF]) are provided in Table 1, Si/Al ratio in Table 2, and trace elements in Table 3.

**Information Values:** Information values are noncertified values that may be of interest and use to the RM user, but insufficient information is available to assess an uncertainty associated with the value [1]. Information values for enthalpy of formation of constituent oxides and liquid water, and elements are provided in Table 4. Information values for unit cell parameters for hydrated ZSM-5 zeolite are provided in Table 5. Information values for particle size distribution are provided in Tables 6 and 8; for refractive index determination in Table 7. In addition, spectra for three types of nuclear magnetic resonance (NMR) analyses are provided in Figures 1 through 3; a plot for particle size distribution is provided in Figure 4; electron microscope images are provided in Figure 5 and information concerning the variation in sample mass with change in ambient humidity is provided in the Appendix.

**Expiration of Reference Values:** The reference values are valid within the measurement uncertainties specified until **31 December 2020**; provided that the RM is handled in accordance with the instructions given in this report (see "Instructions for Use"). The reference values are nullified if the RM is contaminated or modified. The container should be resealed tightly after sampling.

**Maintenance of Reference Values:** NIST will monitor this RM and if substantive changes occur in the reference values, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The overall direction and coordination of the analyses were performed by S. Turner and R.R. Cavanagh of the NIST Surface and Microanalysis Division.

Richard R. Cavanagh, Chief  
Surface and Microanalysis Division

Gaithersburg, MD 20899  
Report Issue Date: 26 July 2006

Robert L. Watters, Jr., Chief  
Measurement Services Division

---

Certain commercial equipment, instruments, or materials are identified in this report to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Analytical measurements were performed at NIST by D.A. Becker, R.A. Fletcher, J.F. Kelly, A.F. Marlow, M.G. Moreno-Ramirez, J.R. Sieber, E.B. Steel, B.H. Toby, S. Turner, J.R. Verkouteren, T.W. Vetter, E.S. Windsor, and R. Zeisler.

NMR studies were performed by G.J. Kennedy and W.S. Borghard at ExxonMobil Research & Engineering in Annandale, NJ. Heat of enthalpy studies were performed by S. Yang and A. Navrotsky at the University of California at Davis.

Statistical consultation for the experimental design and analysis of data was provided by S.D. Leigh, W.F. Guthrie and K.R. Eberhardt of the NIST Statistical Engineering Division.

The zeolite was prepared and packaged by the NIST Measurement Services Division and by Laboratory Quality Services International (LQSI).

The support aspects involved in the preparation and issuance of this RM were coordinated through the NIST Measurement Services Division.

## INSTRUCTIONS FOR USE

**Chemical and Diffraction Analyses:** For comparison to chemical and diffraction values, samples should be equilibrated in a constant relative humidity (RH) of 54 %  $\pm$  2 % for at least 48 h. A hydrator (e.g., glove box) containing a saturated solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with excess salt can attain a constant RH of approximately 54 % when the temperature is 20 °C. ASTM Standard Practice E 104-02 gives more details on maintaining constant RH by means of aqueous solutions [2]. Samples should be in relatively thin layers (< 0.5 cm) in the hydrator.

If samples are to be weighed for chemical analyses, the samples should be equilibrated to approximately 54 % RH and the samples then weighed in the same ambient humidity. This can be accomplished by weighing samples in a glove box containing a scale. For preparation of samples for diffraction analysis, samples should be equilibrated to approximately 54 % RH in a glove box and then sealed within the glove box. The RH of the glove box should be monitored with a calibrated hygrometer. Samples should not be exposed to ambient laboratory humidity prior to weighing for chemical analyses or during the collection of diffraction data. An example of the variation of sample mass with exposure to a different humidity is given in the Appendix. Refer to section on “Chemical Homogeneity Testing by XRF” for minimum recommended mass for chemical analysis.

**Particle Sizing:** For particle sizing experiments, special care must be exercised to obtain subsamples that are representative of the particle size distribution of the entire bottle [3,4,5]. Spin riffling (whole stream rotary sampling) was used to obtain subsamples for characterization of the particle size distribution of this RM. Other methods for subsampling the zeolite material have not been investigated in this study and may result in altered particle size distributions or different uncertainties. In general, the zeolite is highly agglomerated. Therefore, once a representative subsample is obtained, it is recommended that the sample be deagglomerated prior to particle size analysis. Deagglomeration can be achieved by ultrasonification of a suspension of the sample in filtered water. Tests should be run using increasing ultrasonification times to determine the time required to reach a stable particle size distribution. An ice bath may be necessary to reduce the temperature of the suspension during ultrasonification.

## PREPARATION

**Sample Preparation:** The zeolite material came to NIST in a single metal barrel with a porcelain coating. Samples were scooped out of the original container and placed into aluminized bags using an alternate shovel method. By this method, a scoop was taken from the container and placed in a bag; the next scoop taken from the container was placed in another bag, etc. The procedure was repeated until the original container was empty. This procedure was done to ensure that each bag contained samples from all parts of the original container. Each bag contained less than 9 kg (20 lbs) of material. Sample spin riffling and bottling was contracted out to LQSI, which is a division of Commercial Testing & Engineering Co. (CT&E).

## ANALYSES

**Methods Used:** Chemical analyses were performed by X-ray fluorescence spectrometry (XRF), gravimetry, instrumental neutron activation analysis (INAA) of short, medium and long-lived isotopes, magic angle spinning (MAS) NMR, and calorimetric methods.

Unit cell parameters were determined for hydrated samples using synchrotron X-ray diffraction.

Particle size analyses were performed using laser light scattering, laser light extinction, and sedimentation methods. In order to obtain representative samples for the analyses, a series of mass reduction steps were done to randomly chosen units of material using a spin riffling apparatus. Bottles of zeolite were split into 16 subsamples using a spinning riffler. One of the 16 subsamples was then randomly selected and further split into 8 subsamples using a smaller spinning riffler. An overall riffle split mass reduction of 128 yielded samples of approximately 0.2 g, which is the subsample size used for particle analysis. Tests were performed to determine the amount of sonication necessary to ensure deagglomeration of particles and samples were ultrasonified prior to particle size measurements. Images of the particles were obtained by scanning transmission electron microscopy (STEM). Electron microscopy samples were not deagglomerated prior to imaging.

**Chemical Homogeneity Testing by XRF:** Chemical homogeneity was tested for the zeolite for Na, Al, Si, K, Ca, Fe, Zn, and Zr using XRF analysis. No statistically significant differences among bottles were observed for Na, Al, Si, K, Ca, and Fe. A statistical F-test (5 % significance) applied to the data for Zn indicates heterogeneity between bottles at the level of precision of the test data, 0.6 % relative standard deviation for the estimated 0.5 g of material analyzed by the spectrometer. The F-test (5 % significance) applied to the data for Zr indicates heterogeneity between bottles at the level of precision of the test data, 0.8 % relative standard deviation for the estimated 1.0 g of material viewed by the spectrometer. For the major elements, Al and Si, specimens as small as 10 mg will be representative of the bulk material. For the determination of trace elements, the heterogeneity of Zr and Zn must be taken into account and it is recommended that at least 1 g of material be analyzed to obtain results representative of the bulk material.

## REFERENCE VALUES: CHEMISTRY

### Major Components:

Table 1. Reference Values for Major Components of Ammonium ZSM-5 Zeolite

Component	Mass Fraction (%) <sup>(e)(f)</sup>	Methods
Al <sup>(a)</sup>	1.396 ± 0.015	XRF, INAA
Si <sup>(a)</sup>	41.18 ± 0.34	XRF, gravimetry
Si <sup>(b)</sup>	45.19 ± 0.13	gravimetry
LOI <sup>(a)(c)</sup>	8.50 ± 0.09	gravimetry
LOF <sup>(a)(d)</sup>	8.47 ± 0.38	gravimetry

<sup>(a)</sup> Value relative to the hydrated sample mass.

<sup>(b)</sup> Value relative to sample mass ignited at 1000 °C.

<sup>(c)</sup> Ignited at 1000 °C.

<sup>(d)</sup> Fused with Li borates at 1100 °C.

<sup>(e)</sup> The reference values for Al and Si (relative to hydrated mass) are an unweighted mean of the results from two analytical methods. The associated uncertainties are expanded uncertainties about the mean, with coverage factor  $k = 2$  (95 % confidence), calculated by combining a between-method variance [6] with a pooled, within-method variance following the ISO and NIST Guides [7]. Where appropriate, components of uncertainty attributable to fit calibration, balance calibration, blank replication, contamination, mechanical loss, and hydration have been included.

<sup>(f)</sup> The reference values for Si (relative to the ignited sample mass), LOI and LOF are the mean of results obtained by NIST using one analytical method. The expanded uncertainties,  $U$ , for Si (relative to ignited sample mass) and LOI are calculated as  $U = ku_c$  where  $u_c$  is intended to represent, at the level of one standard deviation, the combined standard uncertainty calculated according to the ISO and NIST Guides [7]. The coverage factor,  $k$ , is determined from the Student's  $t$ -distribution with the appropriate associated degrees of freedom for 95 % confidence for each analyte. The expanded uncertainty for LOF is calculated as  $U = ku_c$  where  $u_c$  represents the standard uncertainty of the mean for the NIST values, and  $k = 2.131$  is the Student's  $t$  multiplier corresponding to 95 % confidence for 15 determinations.

## Element Ratios:

Table 2. Reference Value for Atomic Ratio of Si (Relative to Hydrated Sample Mass) to Al<sup>(a)</sup>

Elements	Ratio	Methods
Si/Al	28.34 ± 0.39	XRF, INAA, gravimetry

<sup>(a)</sup> The reference atomic ratio value for Si/Al is calculated using the reference values for the elements from Table 1 and the atomic mass of the elements. The corresponding uncertainties are determined by propagation-of-error [8] for ratios from the unexpanded uncertainties of Table 1, and then expanded by a coverage factor  $k = 2$  (95 % confidence).

## Trace Elements:

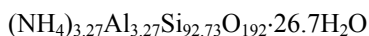
Table 3. Reference Values for Detectable Trace Elements

Element <sup>(a)</sup>	Mass Fraction (mg/kg) <sup>(b)</sup>		
Fe	222.6	±	9.4
Ce	1.708	±	0.051
Co	0.1848	±	0.0051
Cr	4.48	±	0.13
Hf	1.337	±	0.045
La	0.471	±	0.014
Sb	1.581	±	0.045
Sc	0.0943	±	0.0030
Sm	0.0815	±	0.0025
Th	0.335	±	0.0098
W	2.240	±	0.068
Zn	0.749	±	0.048

<sup>(a)</sup> Trace element analyses by INAA were conducted for Ag, As, Au, Cd, Ce, Co, Cr, Cs, Fe, Hf, La, Mo, Rb, Sb, Sc, Se, Sm, Sn, Th, W, and Zn. Several elements assayed were at or below the detection limit achieved for this material with the procedure used. These elements and their detection limits are: Ag (15 µg/kg), As (10 µg/kg), Au (0.2 µg/kg), Cd (0.3 mg/kg), Cs (10 µg/kg), Mo (0.6 mg/kg), Rb (0.1 mg/kg), Se (25 µg/kg), and Sn (2.5 mg/kg). Analysis for Na was conducted by XRF. Na was not detected above the detection limit for the method of 40 mg/kg.

<sup>(b)</sup> The reference value for Fe (relative to hydrated mass) is an unweighted mean of the results from two analytical methods (XRF and INAA). The uncertainty listed with the value is an expanded uncertainty about the mean, with coverage factor  $k = 2$  (95 % confidence), calculated by combining a between-method variance [6] with a pooled, within-method variance following the ISO and NIST Guides [7]. The reference values for trace elements other than Fe are the mean of results obtained by NIST using one analytical method (INAA applied to 16 samples). The expanded uncertainties,  $U$ , are calculated as  $U = ku_c$  where  $u_c$  is intended to represent, at the level of one standard deviation, the combined standard uncertainty calculated according to the ISO and NIST Guides [7]. The coverage factor,  $k$ , is determined from the Student's  $t$ -distribution with the appropriate associated degrees of freedom for 95 % confidence for each analyte.

**Comment 1:** The compositional formula of RM 8852 determined from chemical analyses is:



(NH<sub>4</sub>) is presumed to provide charge balance for the Al content. The LOI value in Table 1 is presumed to include both H<sub>2</sub>O and NH<sub>3</sub>. No crystalline impurities were noted in the diffraction work. The uncertainties for the elemental and water content in the formula for ZSM-5 are: Al ± 0.04, Si ± 0.8, H<sub>2</sub>O ± 0.3. The uncertainties are propagated from the uncertainties in mass fractions given in Table 1. Trace elements have not been included in the formula.

## INFORMATION VALUES: CHEMISTRY

**NMR Analyses for Si Coordination:** The  $^{29}\text{Si}$  MAS NMR spectra obtained from three samples consisted of two main peaks due to  $\text{Si}(\text{OSi})_4$  and  $\text{Si}(\text{OAl})(\text{OSi})_3$ .

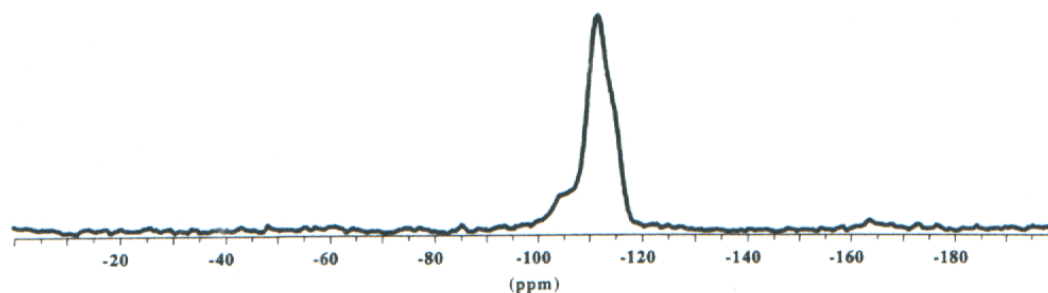


Figure 1.  $^{29}\text{Si}$  MAS NMR spectrum obtained from ZSM-5 zeolite.

**NMR Analyses for Al Coordination:** The  $^{27}\text{Al}$  MAS NMR spectra obtained from three samples exhibited a single resonance at 54.9 ppm corresponding to tetrahedral framework Al. There is no evidence for nonframework, octahedrally coordinated aluminum in this sample.

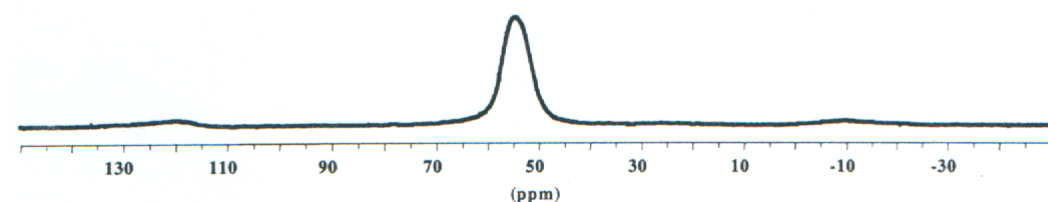


Figure 2.  $^{27}\text{Al}$  MAS NMR spectrum obtained from ZSM-5 zeolite.

**NMR Analyses for H in Proximity to Si:** An example  $^{29}\text{Si}$  cross polarization (CP) MAS NMR spectrum is shown in Figure 3. The CP experiment enhances the signals from those silicon nuclei that are in close proximity to hydrogen, such as covalently bound silanols or trapped hydrocarbons. The signal to noise ratio of a CP-MAS NMR spectrum when compared to that of the  $^{29}\text{Si}$  MAS NMR experiment is a qualitative indicator of the presence of these species.

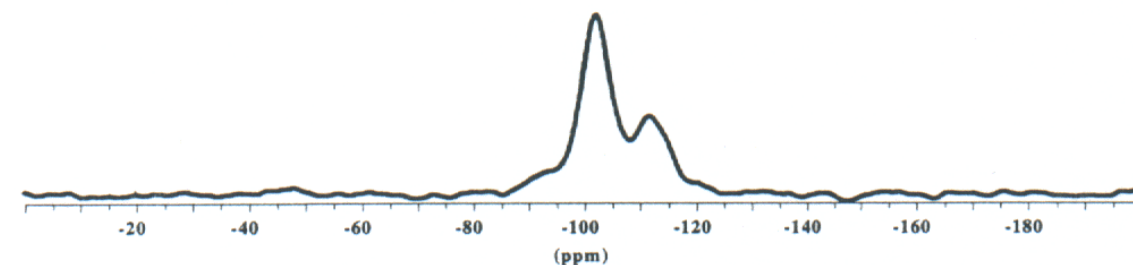


Figure 3.  $^{29}\text{Si}$  CP-MAS NMR spectrum obtained from ZSM-5 zeolite.

### Enthalpy of Formation:

Table 4. Enthalpy of Formation from Constituent Oxides and Liquid Water, and Constituent Elements at 25 °C

Constituents	Enthalpy of Formation (kJ/mol) <sup>(a)</sup>
Oxides and Liquid Water	−6.26 ± 0.54
Elements	−990.8 ± 1.1

<sup>(a)</sup> The uncertainties are propagated from calorimetric data and from literature values for the constituent oxides or elements (coverage factor  $k = 2$ , 95 % confidence).

### INFORMATION VALUES: DIFFRACTION

#### Synchrotron X-ray Diffraction of Hydrated Samples:

Table 5. Unit Cell Parameter of Hydrated Ammonium ZSM-5 Zeolite (Space Group  $Pnma$ )

Axis	Value (nm) <sup>(a)</sup>
$\underline{a}$	2.011 63 ± 0.000 84
$\underline{b}$	1.993 1 ± 0.001 4
$\underline{c}$	1.341 82 ± 0.000 91

<sup>(a)</sup> The uncertainty is one standard deviation based on 16 samples.

**Comment 2:** The unit cell parameters are for information only. The uncertainties for the reported data do not include all sources of biases. For this material, a possible trimodal distribution of unit cell values was obtained.

## INFORMATION VALUES: PARTICLE SIZING

The distributions reported for the particle size measurement methods reported below should be considered valid only for the specific method used. Variations in values among methods may result from effects of particle characteristics such as morphology.

### Laser Light Scattering:

Table 6. Cumulative Volume Percent Less than Particle Diameter of Ten Samples<sup>(a)</sup>

Cumulative Volume (%)	Mean Diameter (μm)	Standard Deviation of the Mean (μm)
5	0.231	0.002
10	0.268	0.002
15	0.298	0.001
20	0.324	0.001
25	0.350	0.001
30	0.375	0.001
35	0.400	0.001
40	0.427	0.001
45	0.454	0.001
50	0.484	0.001
55	0.517	0.002
60	0.553	0.002
65	0.595	0.003
70	0.646	0.004
75	0.712	0.005
80	0.803	0.007
85	0.971	0.012
90	1.698	0.043
95	3.787	0.058

<sup>(a)</sup> Measured by the laser light scattering method.

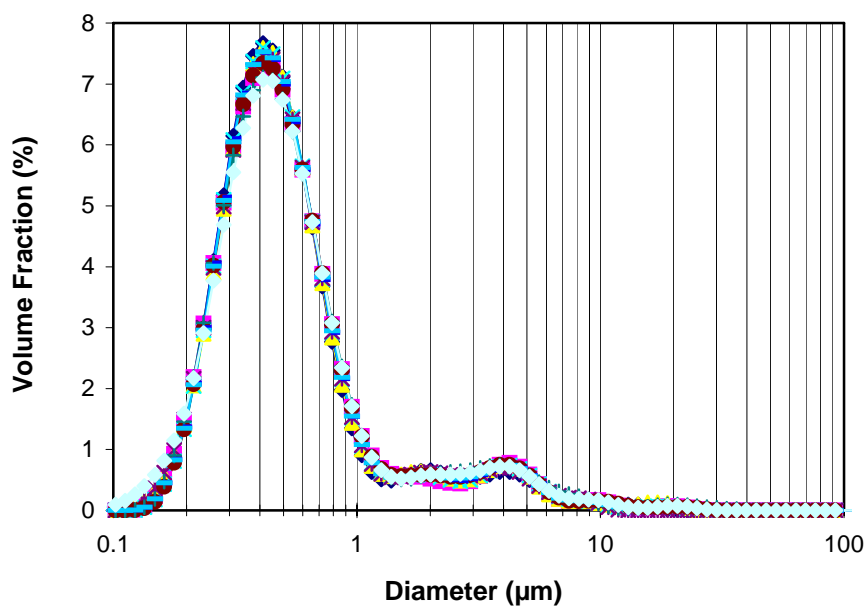


Figure 4. Distribution of differential volume fraction (%) vs. particle diameter as measured by the laser light scattering method. Each curve represents the analysis for a different bottle of the five bottles analyzed.

## Refractive Index Determination for Mie Optical Model:

Table 7. Refractive Index Determination

Refractive Index<sup>(a)</sup>

1.472 to 1.474

<sup>(a)</sup> A value of 1.47 was used in Mie modeling of the particle size distribution for the laser light scattering method since values to 2 decimal places are considered sufficient for this purpose.

**Laser Light Extinction:** The number of particles observed by this method is low and indicates that the bulk of the particles are less than 1  $\mu\text{m}$  in diameter. This is consistent with results for laser light scattering method.

## X-ray Sedimentation:

Table 8. Information Values Obtained by X-ray Sedimentation<sup>(a)</sup>

Cumulative Volume (%)	X-ray Sedimentation Mean Diameter ( $\mu\text{m}$ ) <sup>(b)</sup>	Laser Light Scattering Mean Diameter ( $\mu\text{m}$ ) <sup>(c)</sup>
10	0.21	0.268 $\pm$ 0.002
25	0.30	0.350 $\pm$ 0.001
50	0.45	0.484 $\pm$ 0.001
75	0.74	0.712 $\pm$ 0.005
90	1.41	1.698 $\pm$ 0.043

<sup>(a)</sup> Values from another method for comparison

<sup>(b)</sup> Values for X-ray sedimentation are included for particle diameters less than 0.5  $\mu\text{m}$  but the values are less reliable than those from larger particles due to Brownian motion.

<sup>(c)</sup> Uncertainty values represent the standard deviation of the mean.



STEM:

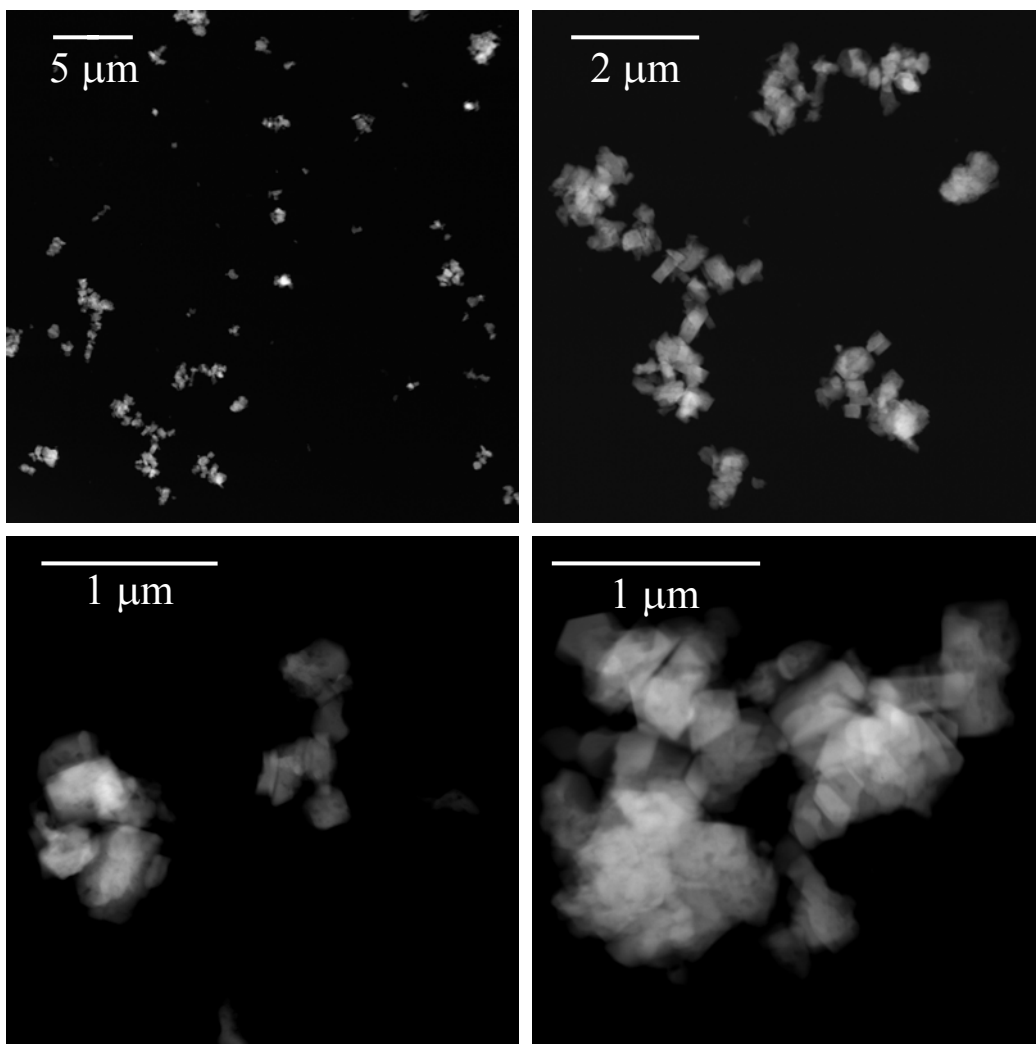


Figure 5. Dark field scanning transmission electron microscopy images of ZSM-5 zeolite.

## REFERENCES

- [1] May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136, U.S. Government Printing Office: Washington, DC (2000); available at: [http://www.cstl.nist.gov/nist839/special\\_pubs/SP260136.pdf](http://www.cstl.nist.gov/nist839/special_pubs/SP260136.pdf).
- [2] ASTM E 104-02; *Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions*; Annu. Book ASTM Stand., Vol. 11.03 (2002).
- [3] Kaye, B.H.; Powder Metall., Vol. 9, pp. 213–234 (1962).
- [4] Allen, T.; Khan, A.A.; Chem. Engr., Vol. 238, pp. CE108–CE112 (1970).
- [5] BS 3406-1; *Methods for Determination of Particle Size Distribution - Part 1: Guide to Powder Sampling*; British Standards Institution, London (1986).
- [6] Levenson, M.S.; Banks, D.L.; Eberhardt, K.R.; Gill, L.M.; Guthrie, W.F.; Liu, H.K.; Vangel, M.G.; Yen, J.H.; Zhang, N.F.; J. Res. Natl. Inst. Stand. Technol., Vol. 105, No. 4, pp. 571–579 (2000).
- [7] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9; International Organization for Standardization: Geneva, Switzerland (1993, revised 1995); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at: <http://physics.nist.gov/Pubs/>.
- [8] Ku, H.H.; J. Res. Natl. Bur. Stand., Vol. 70C, No. 4, pp. 263–273 (1966).

*Users of this RM should ensure that the Report of Investigation in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet at <http://www.nist.gov/srm>.*

## APPENDIX

### Variation in Sample Mass with Change in Ambient Humidity

Experiments were conducted to determine the magnitude of variation in sample mass with change in ambient humidity. One of the experiments is described and its results given as information values so that users of the RM will be aware of the magnitude of mass change with exposure to two relative humidities ( $33 \% \pm 2 \% \text{ RH}$  and  $54 \% \pm 2 \% \text{ RH}$ ).

Approximately 0.85 g of zeolite was placed in an aluminum weighing dish. The sample was placed in a hydrator (in this case, a glass desiccator containing a saturated solution of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with excess salt) and allowed to equilibrate at  $33 \% \pm 2 \% \text{ RH}$  over several days. The hydrator with the sample was placed in a glove box containing a weighing scale and several pans of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  salt in solution. After the glove box reached  $33 \% \pm 2 \% \text{ RH}$ , the sample was removed from the hydrator and the sample mass was determined. The sample was placed back in the hydrator. The pans of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  salt solution in the glove box were exchanged for several pans containing  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  salt solutions. After the glove box was stable at  $54 \% \pm 2 \% \text{ RH}$ , the sample was removed from the hydrator, placed on the scale in the glove box and its mass monitored at one minute intervals for approximately the first hour and periodically over the next several days.

The change in mass for approximately the first hour is shown in Figure A1. The results show a mass difference of approximately 1.2 % between the  $33 \% \pm 2 \% \text{ RH}$  and  $54 \% \pm 2 \% \text{ RH}$  provided by the two salt solutions. The greatest change in mass occurred in the initial few minutes of exposure to  $54 \% \pm 2 \% \text{ RH}$ . After 48 h, the mass gain stabilized at approximately 1.25 %.

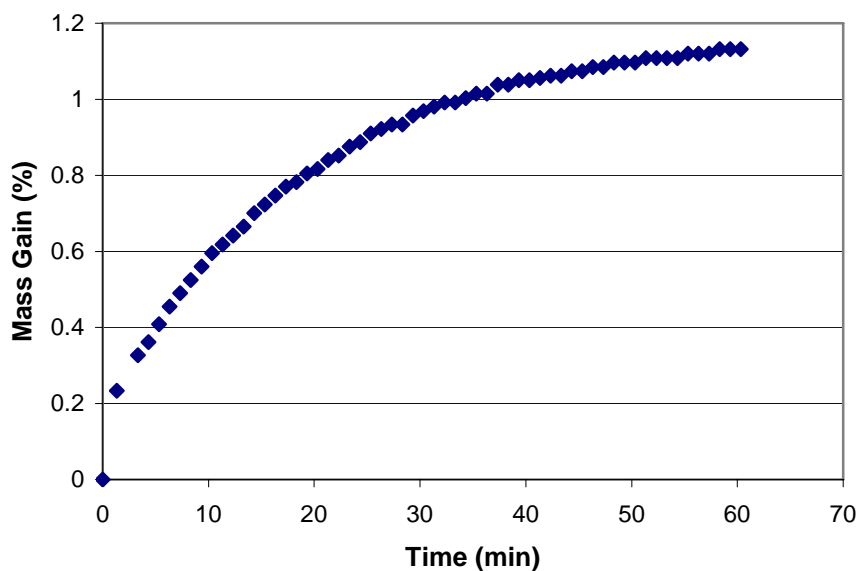


Figure A1. Variation in mass of ZSM-5 zeolite as the ambient humidity was changed from  $33 \% \pm 2 \% \text{ RH}$  (time = 0) to  $54 \% \pm 2 \% \text{ RH}$  (time > 0 min).